Crystal Structures of Dextrorotatory and Racemic Sodium Ammonium Tartrate

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The crystal structures of the title salts, (+)-Na$[NH_4][O_2CCH(OH)CH(OH)CO_2]\cdot 4H_2O$, (+)-(1a), and (±)-Na$[NH_4][O_2CCH(OH)CH(OH)CO_2]\cdot H_2O$, (±)-(1b), have been determined from single-crystal *X*-ray data and refined by least-squares methods to *R* factors of 0.0482 and 0.0452, respectively. The unit-cell dimensions of (+)-(1a) are a = 12.173 9(9), b = 14.412 9(9), c = 6.235 2(9) Å, and Z = 4, space group $P2_12_12$, and of (±)-(1b) a = 15.244(1), b = 5.066 3(7), c = 10.218 6(8) Å, β = 93.60(1)°, and Z = 4, space group $P2_1/a$. Hydrogen bonding in the lattice is found to be more extensive for the (+)-(1a) than for the (±)-(1b) structure, except for the ammonium ion bonding.

THE majority of the synthetic chiral compounds employed in biological applications are racemates, although it has been known from the time of Pasteur [1] that the individual optical isomers in a racemic mixture generally have a differential bioactivity. The use of the more effective optical isomer requires either an asymmetric synthesis or the optical resolution of the corresponding racemate. The principal large-scale method of optical resolution is entrainment, the seeding of a melt or a supersaturated solution of the racemate with a crystal of the required optical isomer.[2] The entrainment procedure is confined to the minor class of racemates which spontaneously resolve on crystallisation, each crystal containing only one of the enantiomers. Recent surveys identify 250 racemates belonging to the spontaneously resolved class.[3]

The comparison of the crystal and molecular structure of an optical isomer with that of the corresponding racemate is relevant to extensions of the entrainment method, and to the general problem of chiral discrimination, particularly, the preferred co-crystallisation of an enantiomer with its optical antipode in the major class of racemates. In a previous study, the molecular packing modes in the crystal of Λ-(−)-tris(pentane-2,4-dionato)chromium(III) and in the corresponding racemic crystal were compared,[4] and a similar study of the racemic and the (*R*)-(−)-1,1′-binaphthyl crystal showed, not only contrasting packing modes in the respective lattices, but also a difference of molecular conformation, *cisoid* in the racemic and *transoid* in the optically active crystal.[5] The crystals previously investigated are essentially molecular, and the present work reports a comparison of the crystal and molecular structure of an ionic and hydrogen-bonded enantiomer crystal with that of the corresponding racemic crystal, sodium ammonium (+)-tartrate, (+)-Na$[NH_4][O_2CCH(OH)CH(OH)CO_2]\cdot 4H_2O$, (+)-(1a), and sodium ammonium tartrate racemate, (±)-Na$[NH_4][O_2CCH(OH)CH(OH)CO_2]\cdot H_2O$, (±)-(1b).

Mitscherlich [6] reported that the crystals of (+)-Na$[NH_4][O_2CCH(OH)CH(OH)CO_2]\cdot nH_2O$ and (±)-Na$[NH_4][O_2CCH(OH)CH(OH)CO_2]\cdot nH_2O$ are isomorphous, and Pasteur [7] accomplished the first optical resolution by crystallising the latter inactive salt at ambient temperature to obtain two morphologically distinct crystal types, distinguished by mirror-image hemihedral facets. Only one of the two types was found to be isomorphous with the (+)-(1a) crystal, giving an identical specific rotation in solution. The second crystal type gave a specific rotation of the same magnitude but of opposite sign, and was identified as (−)-(1a). Scacchi,[8] on crystallising the racemic salt at a higher temperature, obtained a single and different crystal type, morphologically holohedral, containing equivalent quantities of the enantiomeric tartrate ions, (±)-(1b). The transition temperature from the conglomerate of active (+)-(1a) and (−)-(1a) crystals to the racemic (±)-(1b) crystal was found, by dilatometric measurements, to be 27 °C by van't Hoff and van Deventer.[9] The present work refers to the (±)-(1b) crystal of Scacchi [8] and the (+)-(1a) crystal of Mitscherlich [6] and Pasteur.[7]

The molecular and crystal structure of a number of tartrate salts have been determined, notably, those of the sodium rubidium- and rubidium hydrogen-(+)-tartrate crystal,[10,11] in connection with the absolute configuration of (+)-tartaric acid, and of Rochelle salt [12] and its analogues,[13] with reference to the piezoelectric and ferroelectric properties of the crystals. The unit-cell constants have been reported for the (+)-(1a) crystal, which is isomorphous with the corresponding potassium sodium (Rochelle salt) and rubidium sodium salt.[12] The crystal structure of the racemic analogue of Rochelle salt, potassium sodium (±)-tartrate tetrahydrate, has been reported,[14] and corrected,[15] but the structure of the (±)-(1b) crystal has not been investigated previously.

EXPERIMENTAL

Materials and Thermal Studies.—Crystals of (+)-(1a) and (±)-(1b) were grown from aqueous solution at a temperature of 20 and 35 °C, respectively. In each case, aqueous ammonia was added to a solution of the appropriate sodium hydrogen salt until pH *ca.* 8—9 was attained. Both the (+)-(1a) and the (±)-(1b) crystals are efflorescent.

As the racemic salt crystallises into a conglomerate of (+)-(1a) and its antipode below 27 °C, the possibility that this temperature refers to a transition from the tetrahydrate to the monohydrate of the active salt was investigated by differential thermal calorimetry (d.s.c.) and hot-stage microscopy. A d.s.c. scan of (+)-(1a), carried out with a Perkin-Elmer DSC 1B at a heating rate of 2° min^{-1} under nitrogen flushing, revealed no thermal transition between 20 and 52 °C. The latter temperature marked the onset of an endotherm, peaking at 57 °C, which corresponds to the quasi-melting point of a freshly prepared (+)-(1a) crystal measured by rapid heating or with a pre-heated block. The melting essentially represents the dissolution of the salt in the liberated water of hydration. Slow heating or the use of exposed aged crystals results in a higher quasi-melting point, *e.g.* 62 °C for a heating rate of 1° min^{-1} with freshly prepared crystals.

The hot-stage microscopy of (+)-(1a) under silicone oil, carried out with a Meltler FP52 instrument at a heating rate of 2° min^{-1}, showed no changes in the crystal morphology or the birefringence over the 20 to 40 °C range. At 52—53 °C wetting of the crystal was observed, and the growth of fine needles from the crystal commenced at 56 °C. Crystals of (+)-(1a) maintained for 2.5 h at 70—85 °C lose two of the water molecules of hydration at atmospheric pressure, and three under 30 mmHg * pressure. The formation of (+)-(1b) in the latter case was confirmed by elemental analysis of the dried product.

The crystal of (±)-(1b) is the more efflorescent and, on heating, the crystal becomes progressively more opaque, without ' melting ', but with some wetting. Neither of the anhydrous salts melts below 150 °C, above which the salts gradually discolour and decompose.

X-Ray Crystallography.—In order to avoid the loss of water of hydration, each of the crystals, (+)-(1a) and (±)-(1b) was sealed in a capillary tube for the *X*-ray diffraction measurements. The unit-cell parameters of each crystal were determined from Weissenberg photographs and subsequently were refined on a diffractometer. The axial ratios found are in good agreement with the corresponding macroscopic ratios, determined by crystallometry, reported by Groth.[16] The unit-cell constants found for (+)-(1a) are in agreement to three significant figures with the corresponding values reported by Beevers and Hughes [12] in 1941, except for the *c* edge (6.18 Å), determined by layer-line measurements only in the latter work.

Crystal data. (*i*) (+)-(1a). Na(NH$_4$) (+)-C$_4$H$_4$O$_6$·4H$_2$O, $M = 261.2$, Orthorhombic, $a = 12.173\,9(9)$, $b = 14.412\,9(9)$, $c = 6.235\,2(9)$ Å, $U = 1\,094.04$ Å^3, $D_m = 1.59$, $Z = 4$, $D_c = 1.585$ g cm^{-3}, $F(000) = 552$, Cu-K_α radiation, $\lambda = 1.541\,78$ Å, μ(Cu-K_α) = 15.9 cm^{-1}, space group $P2_12_12$.

(*ii*) (±)-(1b). Na(NH$_4$) (±)-C$_4$H$_4$O$_6$·H$_2$O, $M = 207.2$, Monoclinic, $a = 15.244(1)$, $b = 5.066\,3(7)$, $c = 10.218\,6(8)$ Å, $\beta = 93.60(1)°$, $U = 787.63$ Å^3, $D_m = 1.75$, $Z = 4$, $D_c = 1.746$ g cm^{-3}, $F(000) = 432$, Cu-K_α radiation, $\lambda = 1.541\,78$ Å, μ(Cu-K_α) = 17.8 cm^{-1}, space group $P2_1/a$.

Structure determination. Intensity data were collected on an Enraf-Nonius CAD-4 automatic diffractometer operated in the 2θ—θ scan mode up to θ = 70°. The structures of both the (+)-(1a) and the (±)-(1b) crystals were solved by the direct method, the heavy-atom method being employed additionally in the former case, and both structures were refined by the full-matrix least-squares procedure. All of the hydrogen atoms progressively appeared at successive stages of the refinement and the subsequent differential Fourier synthesis. The atomic scattering factors for the hydrogen atoms and for the heavier atoms were taken from refs. 17 and 18, respectively. The intensity data were not corrected for absorption, and all of the structure factors, for each of the crystals, were assigned a unit weight. The calculations were carried out by means of the University of London CDC 6600 and 7600 computers, employing the programs SHELX 76, MULTAN 78, and *X*-RAY 72.

TABLE 1

Fractional atomic co-ordinates * (×10^3 for hydrogen, ×10^4 for the heavier atoms) with estimated standard deviations in parentheses

(*i*) (+)-(1a)	*x*	*y*	*z*
O(1)	6 218(2)	6 103(2)	3 508(5)
O(2)	7 099(3)	7 007(2)	1 148(5)
O(3)	6 726(3)	8 551(2)	3 224(5)
O(4)	7 951(2)	7 473(2)	6 298(5)
O(5)	7 311(3)	9 040(2)	8 160(5)
O(6)	5 562(3)	8 592(2)	8 363(5)
C(1)	6 571(3)	6 876(2)	2 821(6)
C(2)	6 312(3)	7 733(3)	4 197(6)
C(3)	6 805(3)	7 626(2)	6 438(6)
C(4)	6 534(4)	8 486(2)	7 782(6)
H(1)	552(3)	777(3)	418(7)
H(2)	648(5)	710(3)	733(10)
H(3)	724(5)	836(5)	217(10)
H(4)	823(6)	804(5)	701(14)
Na	7 301(1)	4 917(1)	5 174(3)
N(1)	5 000	0	1 392(9)
H(11)	553(6)	18(5)	244(11)
H(12)	533(5)	−58(5)	54(12)
N(2)	5 000	5 000	495(12)
H(21)	551(6)	443(5)	−156(13)
H(22)	446(6)	458(5)	126(12)
W(3)	4 323(3)	7 035(3)	9 507(8)
H(31)	479(5)	753(4)	975(13)
H(32)	361(4)	726(6)	934(16)
W(4)	7 424(3)	5 399(2)	8 793(5)
H(41)	713(6)	584(7)	953(16)
H(42)	760(5)	499(5)	986(11)
W(5)	4 253(3)	6 027(3)	5 696(9)
H(51)	433(5)	635(4)	705(10)
H(52)	491(7)	578(5)	532(12)
W(6)	3 907(2)	9 165(2)	5 195(6)
H(61)	417(6)	908(5)	671(8)
H(62)	349(6)	861(5)	515(13)
(*ii*) (±)-(1b)	*x*	*y*	*z*
Na	7 118(0)	4 660(2)	3 160(1)
O(1)	8 589(1)	4 450(3)	2 804(2)
O(2)	9 146(1)	1 283(3)	4 123(2)
O(3)	10 798(1)	2 701(3)	3 873(1)
O(4)	10 126(1)	1 830(3)	1 160(1)
O(5)	11 809(1)	3 616(3)	1 381(1)
O(6)	11 354(1)	7 755(3)	1 645(1)
C(1)	9 207(1)	3 241(4)	3 405(2)
C(2)	10 140(1)	4 282(4)	3 208(2)
C(3)	10 294(1)	4 325(4)	1 740(2)
C(4)	11 231(1)	5 320(4)	1 568(2)
H(1)	1 018(1)	625(1)	361(1)
H(2)	984(1)	566(1)	124(1)
H(3)	1 053(2)	171(6)	439(3)
H(4)	1 057(2)	49(6)	145(3)
N(1)	8 445(1)	−997(4)	1 096(2)
H(11)	797(2)	−27(7)	127(3)
H(12)	893(2)	−17(6)	102(3)
H(13)	834(3)	−186(7)	23(4)
H(14)	853(2)	−250(5)	180(2)
W(2)	7 476(1)	3 739(3)	5 679(2)
H(21)	784(2)	499(6)	559(3)
H(22)	705(2)	467(6)	572(3)

* W(*n*) = Water molecules; W(*n*)—H(*n*1) and W(*n*)—H(*n*2) represent the O–H bonds within a molecule.

The final *R* factors of 0.0482 and 0.0452 for (+)-(1a) and (±)-(1b), respectively, were based upon the reflections with $|F_o| \geqslant 3\sigma(F_o)$ [1 170 out of 1 209 observed unique reflections for (+)-(1a) and 1 395 out of the corresponding 1 466 reflections for (±)-(1b)]. The final atomic parameters with estimated standard deviations are listed for each of the two structures in Table 1. Observed and calculated structure

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

amplitudes and the thermal parameters of the atoms are tabulated in Supplementary Publication No. SUP 23033 (15 pp.).*

DISCUSSION

Molecular Structures.—Apart from the absolute configuration of one-half of the tartrate ions in the (±)-(1b) crystal, the structure of the dianion differs significantly between the two crystals only in the orientation of a single hydroxyl group, that containing the oxygen atom O(4) (Figure 1), the corresponding bond lengths and bond angles being otherwise similar (Table 2). The four carbon atoms of the tartrate ion are nearly coplanar in each of the two crystals, as are the atoms of each carboxylate group and the bonded α-carbon atom. The equations of the mean planes, and the deviation of each atom from its associated plane, are listed for the two structures in Table 3, together with the dihedral angle between the planes in a given ion.

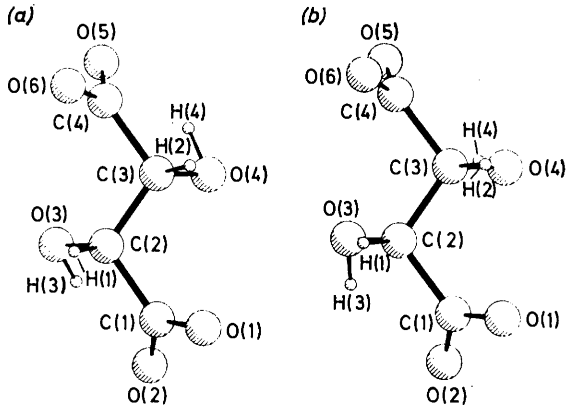

FIGURE 1 Structure of the (+)-tartrate molecules in (*a*) the (+)-(1a) and (*b*) the (±)-(1b) crystals

In the active crystal, (+)-(1a), the carboxylate group planes are so disposed that one of the constituent oxygen atoms and the adjacent hydroxyl group, bonded to the α-carbon atom, form an intramolecular hydrogen bond, with O(2) · · · O(3) = 2.613 and O(4) · · · O(5) = 2.655 Å (Figure 1). In the racemic structure of (±)-(1b) only one of the hydroxyl groups of a tartrate ion forms a similar intramolecular hydrogen bond [O(2) · · · O(3) = 2.646 Å], while the other hydroxyl group is directed towards another tartrate ion, related by a translation along the *b* crystal axis, and forms an intermolecular hydrogen bond [O(4) · · · O(6)′ = 2.810 Å] (Table 4).

The two C–O bond lengths of a given carboxylate group are significantly inequivalent in both structures (Table 2). In each case the oxygen atom of the longer C–O bond is located the closer to a sodium or ammonium cation. The two C–O bond lengths of a carboxylate group are approximately equal in the structure[13] of lithium ammonium (+)-tartrate monohydrate.

Crystal Structure of (+)-(1a).—The structure of the active crystal is characterised by a two-dimensional chiral network of intermolecular bonds in the *ab* crystal plane, shown by a projection of the structure on a plane perpendicular to the *c* axis (Figure 2). The tartrate ions related by a 2_1 screw axis along the crystal *a* axis are linked by hydrogen bonds through water molecules, W(*n*), forming infinite chains, O(4)(tartrate)O(6) · · · H–W(6)–H · · · O(4)(tartrate)O(6) · · · H–W(6)–H. The tartrate ions related by a 2_1 screw axis along the crystal *b* axis are similarly hydrogen-bonded through other water molecules in the catenation, O(2)(tartrate)O(5) · · · H–W(4)–H · · · O(2)(tartrate)O(5) · · · H–W(4)–H. Additional intermolecular hydrogen bonding along the (1 1 0)

TABLE 2

Intramolecular bond lengths (Å) and angles (°)

	(+)-(1a)	(±)-(1b)
O(1)–C(1)	1.269(3)	1.253(2)
O(2)–C(1)	1.239(4)	1.241(3)
C(1)–C(2)	1.537(4)	1.541(2)
C(2)–H(1)	0.97(3)	1.08(1)
C(2)–O(3)	1.418(3)	1.423(2)
O(3)–H(3)	0.95(3)	0.85(3)
C(2)–C(3)	1.528(3)	1.532(2)
C(3)–H(2)	1.02(1)	1.08(1)
C(3)–O(4)	1.415(3)	1.413(2)
O(4)–H(4)	0.99(5)	0.99(3)
C(3)–C(4)	1.533(4)	1.536(2)
C(4)–O(5)	1.259(4)	1.257(2)
C(4)–O(6)	1.247(4)	1.249(2)
O(1)–C(1)–O(2)	126.4(3)	126.8(2)
O(1)–C(1)–C(2)	116.6(2)	116.1(2)
O(2)–C(1)–C(2)	117.0(2)	117.1(2)
C(1)–C(2)–O(3)	110.8(2)	111.9(1)
C(1)–C(2)–C(3)	110.4(2)	109.4(1)
C(2)–O(3)–H(3)	107(3)	106(2)
O(3)–C(2)–C(3)	109.7(2)	109.2(1)
C(2)–C(3)–O(4)	110.3(2)	111.3(1)
C(3)–O(4)–H(4)	100(3)	113(2)
O(4)–C(3)–C(4)	111.8(2)	113.0(1)
C(2)–C(3)–C(4)	109.5(2)	111.3(1)
C(3)–C(4)–O(5)	117.0(3)	117.3(1)
C(3)–C(4)–O(6)	117.5(3)	117.0(1)
O(5)–C(4)–O(6)	125.5(3)	125.7(2)

	(+)-(1a)		(±)-(1b)
N(1)–H(11)	0.95(5)	N(1)–H(11)	0.84(4)
N(1)–H(12)	1.07(5)	N(1)–H(12)	0.85(3)
H(11)–N(1)–H(11)′	94(6)	N(1)–H(13)	0.99(4)
H(11)–N(1)–H(12)	108(4)	N(1)–H(14)	1.05(2)
H(12)–N(1)–H(12)′	121(6)	H(11)–N(1)–H(12)	124(3)
		H(11)–N(1)–H(13)	107(3)
N(2)–H(21)	1.11(5)	H(11)–N(1)–H(14)	104(3)
N(2)–H(22)	1.01(5)	H(12)–N(1)–H(13)	103(3)
H(21)–N(2)–H(21)′	137(6)	H(12)–N(1)–H(14)	110(2)
H(21)–N(2)–H(22)	95(4)	H(13)–N(1)–H(14)	108(2)
H(22)–N(2)–H(22)′	124(6)		
W(3)–H(31)	0.93(3)	W(2)–H(21)	0.86(3)
W(3)–H(32)	0.94(4)	W(2)–H(22)	0.80(3)
H(31)–W(3)–H(32)	109(5)	H(21)–W(2)–H(22)	96(3)
W(4)–H(41)	0.87(7)		
W(4)–H(42)	0.92(3)		
W(41)–W(4)–H(42)	101(6)		
W(5)–H(51)	0.97(4)		
W(5)–H(52)	0.92(6)		
H(51)–W(5)–H(52)	110(4)		
W(6)–H(61)	1.00(3)		
W(6)–H(62)	0.95(6)		
H(61)–W(6)–H(62)	95(4)		

Primed atoms are related to the corresponding unprimed atoms by a two-fold rotation.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

direction through the NH_4^+ ion links the tartrate ion related by the two-fold rotation axis of symmetry. No hydrogen bonds connect the individual two-dimensional intermolecular hydrogen-bonded arrays in the crystal *ab* plane. The layers in the *ab* plane are linked primarily by the sodium ions. Each sodium ion is co-ordinated to six oxygen atoms, five belonging to water molecules and tartrate ions in one layer and the sixth to a water molecule in the adjacent layer sandwiching the sodium ion (Table 4). There are two independent ammonium ions in the crystal structure, located at sites of C_2 symmetry. Only two of the four hydrogen atoms of each ammonium ion form relatively strong hydrogen bonds (Table 4). One of the two independent ammonium ions forms further weaker hydrogen bonds [N(1) · · · W(6) = 2.973 Å], but the next nearest neighbour of the other independent ammonium ion is too distant to appreciably hydrogen-bond [N(2) · · · W(3) = 3.108 Å].

TABLE 3

Equations of the mean planes: x, y, and z are fractional co-ordinates, with deviations from the planes in Å ($\times 10^4$)

(*i*) (+)-(1a)

Plane I: $10.250x + 6.316y - 1.962z = 10.530$
C(1), −15, C(2), 15, C(3), 14, C(4), −15

Plane II: $10.402x - 1.905y + 3.133z = 6.408$
C(2), 2, C(1), 7, O(1), 3, O(2), 2

Plane III: $-2.469x + 7.290y - 5.228z = 0.514$
C(3), 30, C(4), −112, O(5), 41, O(6), 41

dihedral angles (°) between the planes

	II	III
I	59.8	71.7
II		48.6

(*ii*) (±)-(1b)

Plane I: $5.250x - 4.747y + 0.3818z = 3.423$
C(1), 69, C(2), −70, C(3), −68, C(4), 69

Plane II: $-1.768x + 3.074y + 0.094z = 2.119$
C(2), −7, C(1), 27, O(1), −10, O(2), −10

Plane III: $2.161x - 0.396y + 9.973z = 3.785$
C(3), 13, C(4), −49, O(5), 18, O(6), 18

dihedral angles (°) between the planes

	II	III
I	55.9	79.6
II		44.6

Of the four water molecules of hydration, W(3) and W(5) form only one significant hydrogen bond per molecule, additional to the hydrogen bond linking the two molecules (Table 4), and it is probable that these represent the two water molecules of hydration lost on heating the (+)-(1a) crystal to *ca.* 80 °C at atmospheric pressure. The two other water molecules of hydration, W(4) and W(6), each form two hydrogen bonds linking tartrate ions, setting up the infinite hydrogen-bonded chains along the *b* and the *a* crystal axes, respectively. While both of the hydrogen bonds to W(4) are strong, one of the two hydrogen bonds to W(6) is weak (Table 4), and it is probable that W(6) is the third water molecule of hydration lost on heating the (+)-(1a) crystal to *ca.* 80 °C under reduced pressure.

Crystal Structure of (±)-(1b).—The intermolecular hydrogen bonding in the racemic crystal, (±)-(1b), is dominated by the ammonium ion (Figure 3). Each ammonium ion links an enantiomorphous pair of tartrate ions, forming an infinite chain along the direction of the crystal *a* axis with the hydrogen bonding, O(4)[(+)-tartrate]O(5) · · · H–N–H · · · O(4)[(−)-tartrate]O(5) · · · H–N–H. A third hydrogen atom of each ammonium ion hydrogen-bonds to the oxygen atom O(1) of a tartrate ion in an adjacent parallel infinite chain, displaced along the direction of the crystal *b* axis from the chain containing the ammonium ion, thus forming a network of hydrogen bonds in the *ab* plane. Two neighbouring networks are staggered relative to one another, and are linked by hydrogen bonds between the remaining, fourth, hydrogen atom of the ammonium ion in one *ab* network and the oxygen atom O(5) of a tartrate ion in the other array. Each network pair in a plane parallel

TABLE 4

Dimensions of the hydrogen bonds and other close contacts

(*i*) (+)-(1a)

A B	B at *	A–B/ Å	H–B/ Å	A–H · · · B/ °
O(4)–H(4) · · · O(5)	I(0 0 0)	2.655	1.95	126
O(3)–H(3) · · · O(2)	I(0 0 0)	2.613	2.06	116
N(1)–H(12) · · · O(6)	I(0 $\bar{1}$ $\bar{1}$)	2.855	1.83	160
N(2)–H(22) · · · O(1)	II(1 1 0)	2.874	1.90	160
W(3)–H(31) · · · O(6)	I(0 0 0)	2.797	1.99	144
W(4)–H(41) · · · O(2)	I(0 0 1)	2.773	1.96	156
W(4)–H(42) · · · O(5)	III(1 $\bar{1}$ 2)	2.748	1.84	169
W(5)–H(51) · · · W(3)	I(0 0 0)	2.786	1.83	173
W(5)–H(52) · · · O(1)	I(0 0 0)	2.756	2.00	139
W(6)–H(61) · · · O(6)	I(0 0 0)	2.940	2.11	139
W(6)–H(62) · · · O(4)	IV($\bar{1}$ 1 1)	2.792	1.92	152
Na · · · O(5)	III(1 $\bar{1}$ 1)	2.478		
Na · · · O(3)	III(1 $\bar{1}$ 1)	2.506		
Na · · · O(1)	I(0 0 0)	2.396		
Na · · · W(4)	I(0 0 0)	2.366		
Na · · · W(5)	II(1 1 0)	2.353		
Na · · · W(6)	IV(0 1 1)	2.373		

(*ii*) (±)-(1b)

A B	B at †	A–B/ Å	H–B/ Å	A–H · · · B/ °
O(3)–H(3) · · · O(2)	I(0 0 0)	2.646	2.12	120
O(4)–H(4) · · · O(6)	I(0 $\bar{1}$ 0)	2.810	1.83	169
N(1)–H(11) · · · O(5)	IV(0 1 0)	2.801	1.97	171
N(1)–H(12) · · · O(4)	I(0 0 0)	2.933	2.09	171
N(1)–H(13) · · · O(5)	III(2 0 0)	2.863	1.87	177
N(1)–H(14) · · · O(1)	I(0 $\bar{1}$ 0)	2.892	1.86	169
W(2)–H(22) · · · O(2)	III(1 0 1)	2.807	2.01	168
W(2) · · · W(2)	II (1 0 1)	2.892		
O(2) · · · O(3)	III(2 0 1)	2.872		
Na · · · O(1)	I(0 0 0)	2.296		
Na · · · O(3)	IV(0 1 0)	2.489		
Na · · · O(5)	IV(0 1 0)	2.485		
Na · · · O(6)	IV(0 2 0)	2.290		
Na · · · W(2)	II(1 0 1)	2.443		
Na · · · W(2)	I(0 0 0)	2.639		

* The Roman numerals indicate symmetry operations: I x, y, z; II $-x, -y, z$; III $0.5 - x, 0.5 + y, -z$; IV $0.5 + x, 0.5 - y, -z$.

† The Roman numerals indicate symmetry operations: I x, y, z; II $0.5 - x, 0.5 + y, -z$; III $-x, -y, -z$; IV $0.5 + x, 0.5 - y, z$.

to the crystal *ab* plane constitutes a closed system in that it is not hydrogen-bonded to its neighbouring analogues. The linkage between the network pairs is provided primarily by the sodium ions and water molecules co-ordinated to them. Each sodium ion is co-ordinated to four oxygen atoms of tartrate ions and to two water molecules (Figure 3, Table 4).

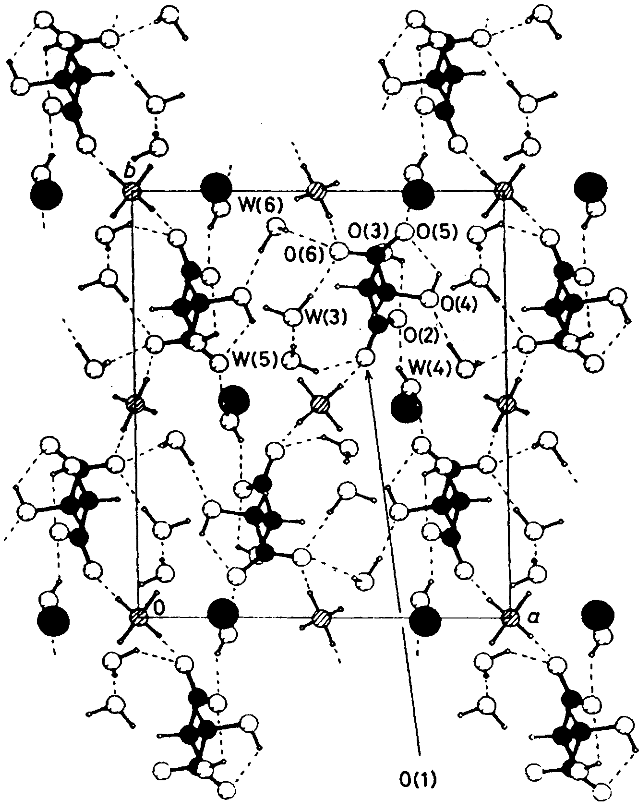

FIGURE 2 Projection of the (+)-(1a) crystal structure on the *ab* plane. Hydrogen bonds are indicated by broken lines

Crystal Structure Comparison.—The (+)-(1a) crystal belongs to the space group $P2_12_12$ which allows a packing of maximum density for an array of one of the two optical isomers of a chiral molecule with C_2 symmetry.[19] The space group $P2_1/a$ of the (±)-(1b) crystal is one of the four [19] permitting a closest-packed lattice of centrosymmetric units, notably, inversion-paired optical antipodes in a racemate. The different degrees of hydration of the (+)-(1a) and the (±)-(1b) crystal preclude a direct packing-density comparison of the two structures, but a limited comparison becomes feasible with the assumption that the effective density of the water of hydration is unity in both crystals. Subtraction of the volume occupied by water molecules from the unit cell of each crystal indicates that the sodium, ammonium, and tartrate ions in the asymmetric unit take up 167 Å^3 in the racemic structure but only 154 Å^3 in the optically active lattice. The contrast, which suggests a more economic packing of the ions in the active structure, is dependent upon the assumed unit density of the water of hydration and it arises in large measure from the greater extent of hydrogen bonding in the (+)-(1a) structure, compared to the (±)-(1b) lattice, due to the water molecules subtracted out for the volume estimates.

The major distinction between the active and the racemic sodium ammonium tartrate crystal structure lies in the degree to which each tartrate ion is hydrogen-bonded. Each tartrate ion possesses two hydrogen-donor and four hydrogen-acceptor functions. Both of the donor functions are exercised in intramolecular hydrogen bonding in the (+)-(1a) structure, whereas the acceptor functions participate in eight intermolecular as well as the two intramolecular hydrogen bonds. In the lattice of (±)-(1b) the acceptor and the donor functions of each tartrate ion take part in only one intramolecular and six intermolecular hydrogen bonds. The water molecule of the (±)-(1b) structure exercises only a single donor function, whereas two of the four water molecules in the (+)-(1a) lattice engage both of their donor functions, while the other two water molecules employ three of the total of four donor functions (Table 4). Only the ammonium ion is the more completely hydrogen-bonded in the racemic lattice, disposing all four donor

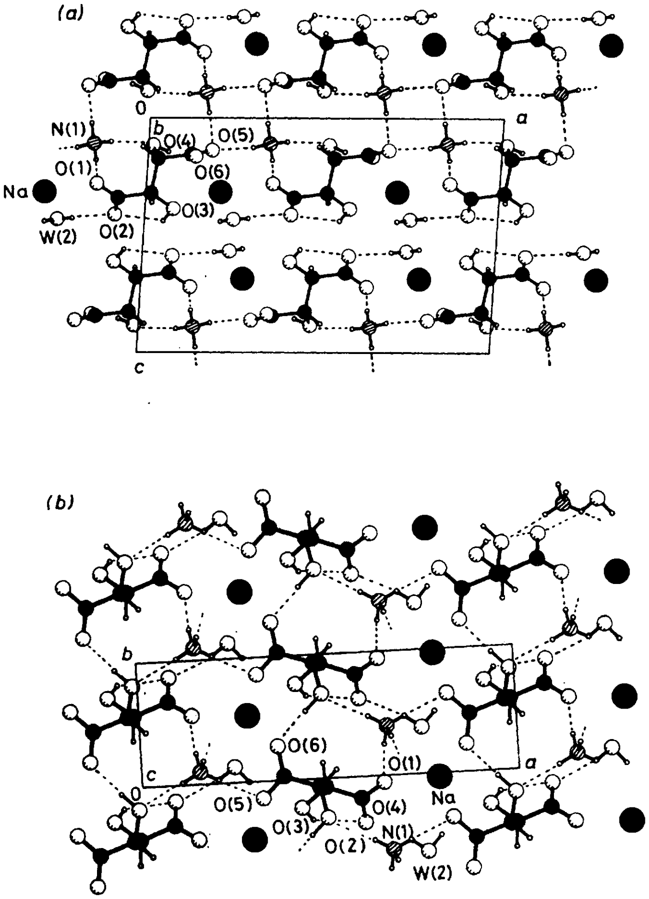

FIGURE 3 Projection of the (±)-(1b) crystal structure on (*a*) the *ac* plane and (*b*) the *ab* plane with $0.5 < z < 1.0$, showing the hydrogen bonding

functions, compared with primarily two donor functions in the chiral (+)-(1a) structure.

The (+)-(1a) crystal is not only isomorphous but also isostructural with the analogous sodium potassium salt,[12] (+)-$NaK[O_2CCH(OH)CH(OH)CO_2]\cdot4H_2O$ (Rochelle salt). The crystal structure of the corresponding racemate, also a tetrahydrate, which is triclinic, belonging to the space group $P\bar{1}$, has been analysed [14] to display the features common to the active and racemic lattices. The comparison is limited, however, by a revision [15] of the hydrogen-bonding structure earlier described.[14] From solubility measurements, van't Hoff and Goldschmidt [20] reported the spontaneous resolution of the racemate, formulated as (±)-$NaK[O_2CCH(OH)CH(OH)CO_2]\cdot3H_2O$ into a conglomerate of (+)-$NaK[O_2CCH(OH)CH(OH)CO_2]\cdot4H_2O$ and its antipode at the transition temperature of −6 °C.

The solubility *versus* temperature relations for the lithium ammonium salts of racemic and (+)-tartaric acid extrapolate to an intersection at −62 °C, suggesting the hypothetical resolution of the racemate into a conglomerate of active crystals at lower temperatures.[21] Although the active crystal [13] (+)-$Li[NH_4][O_2CCH(OH)CH(OH)CO_2]\cdot H_2O$ belongs to the same space group, $P2_12_12$, as (+)-(1a), there are limited analogies between the two crystal structures. The unit cell [13] *b* and *c* edges of the lithium ammonium salt ($a = 7.878$, $b = 14.642$, and $c = 6.426$ Å) are similar to the corresponding cell constants of (+)-(1a), but the *a* cell length is substantially shorter, due to the smaller co-ordination sphere of the lithium ion, relative to that of the sodium ion. The shorter *a* cell length of the lithium ammonium salt allows the direct hydrogen bonding of different tartrate ions, and the formation of hydrogen bonds between two independent ammonium ions and a single carbonyl oxygen atom.[13] Although both are monohydrates, (±)-(1b) and (+)-$Li[NH_4][O_2CCH(OH)CH(OH)CO_2]\cdot H_2O$ form intermolecular hydrogen-bonding networks with as few analogies as those between the corresponding networks of the latter crystal and of (+)-(1a).

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REFERENCES

[1] L. Pasteur, *Res. Mol. Asym.*, 1860, Alembic Club Reprint, no. 14, Livingstone, Edinburgh, 1948.
[2] S. H. Wilen, A. Collet, and J. Jacques, *Tetrahedron*, 1977, **33**, 2725.
[3] A. Collet, M. J. Brienne, and J. Jacques, *Bull. Soc. Chim. Fr.*, 1972, 127; 1974, 494; *Chem. Rev.*, 1980, **80**, 215.
[4] R. Kuroda and S. F. Mason, *J. Chem. Soc., Dalton Trans.*, 1979, 273.
[5] R. Kuroda and S. F. Mason, *J. Chem. Soc., Perkin Trans. 2*, 1981, 167.
[6] E. Mitscherlich, *Compt. Rend.*, 1844, **19**, 719.
[7] L. Pasteur, *Compt. Rend.*, 1849, **28**, 477.
[8] A. Scacchi, *Atti Accad. Sci. Napoli, Cl. Sci. Fis. Mat.*, 1865, **4**, 250.
[9] J. H. van't Hoff and C. M. van Deventer, *Z. Phys. Chem.*, 1887, **1**, 165.
[10] J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature*, 1951, **168**, 271.
[11] A. J. van Bommel and J. M. Bijvoet, *Acta Crystallogr.*, 1958, **11**, 61.
[12] C. A. Beevers and W. Hughes, *Proc. Roy. Soc. London*, 1941, **A177**, 251.
[13] H. Hinazumi and T. Mitsui, *Acta Crystallogr., Sect. B*, 1972, **28**, 3299; *Sect. A*, 1972, **28**, S185 and S186.
[14] R. Sadanaga, *Acta Crystallogr.*, 1950, **3**, 416.
[15] J. R. Clark, *Acta Crystallogr.*, 1964, **17**, 459.
[16] P. Groth, 'Chemische Krystallographie,' Englemann, Leipzig, 1910, vol. 3, pp. 333 and 371.
[17] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
[18] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1968, vol. 4.
[19] A. I. Kitaigorodsky, 'Molecular Crystals and Molecules,' Academic Press, London, 1973, p. 34.
[20] J. H. van't Hoff and H. Goldschmidt, *Z. Phys. Chem.*, 1895, **17**, 505.
[21] A. N. Campbell and L. Slotin, *J. Am. Chem. Soc.*, 1933, **55**, 3961.